

Figure 2 Asymmetric double-well potential hypersurfaces of the ground and excited states of guanine. q is a geometrical variable mainly constituted by folding of the rings. The arrow shows a poor Frank-Condon factor of the (0,0) band region.

It is clear that the strong intensity dip observed in the solution spectrum of guanine around 260 nm does not account for two systems joining each other in this region. Instead, the dip appears to be due to the asymmetric double-well nature of the ground and excited state potential surfaces of the molecule and poor Frank-Condon factor of the (0,0) band region of the spectrum as illustrated in figure 2. This is confirmed by the fact that the strong dip in intensity observed in the solution spectrum of guanine does not appear in the spectrum of the film. The asymmetric double-well potentials are caused by non-planarity of free guanine, its rings being folded at the CC double bond and change in ring folding to the other side of the plane (of planar geometry) following excitation. This possibility is supported by earlier theoretical work on guanine and other bases as well as x-ray crystallographic work on certain purines²⁻⁴. It appears that the molecule becomes planar in the film in both the ground and excited states. This agrees with the results obtained by x-ray crystallography¹. Non-planarity and flexibility of guanine with respect to folding of the rings at the CC double bond has been recently suggested to be of crucial significance in making this base specially suitable for attack by

aromatic hydrocarbon carcinogens which act via intercalation in DNA⁴.

16 April 1985

1. Voet, D. and Rich, A., *Proc. Nucl. Acid Res. Mol. Biol.*, 1970, **10**, 183.
2. Sletten, J. and Jensen, L. H., *Acta Crystallogr.*, 1969, **B25**, 1608.
3. Subramanian, E. and Marsh, R. E., *Acta Crystallogr.*, 1971, **B27**, 753.
4. Mishra, P. C., In: *Molecular basis of cancer*, (ed.) R. Rein, Alan R. Liss Inc., New York, 1984.
5. Callomon, J. H., Dunn, T. M. and Mills, I. M., *Philos. Trans. R. Soc., (London)*, 1966, **A259**, 499.
6. Callis, P. R. and Rosa, E. J., *J. Am. Chem. Soc.*, 1964, **86**, 2292.

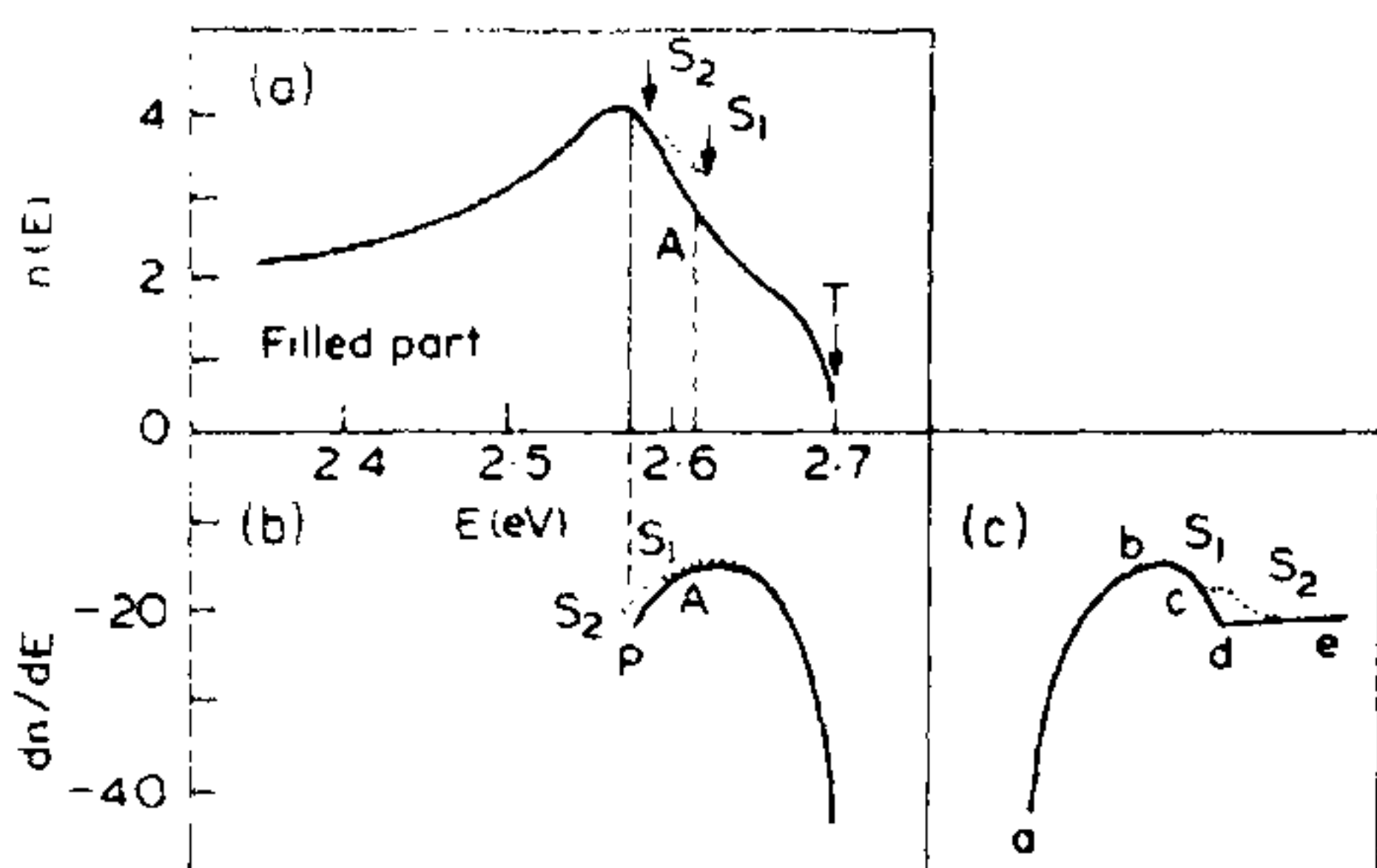
HYDROGEN DIFFUSION IN LOW TEMPERATURE ANNEALED NICKEL

NAMITA KAPOOR and A. N. NIGAM

Physics Department, Harcourt Butler Technological Institute, Kanpur 208 002, India.

THERMOELECTRIC studies of cathodically hydrogenated nickel wires which were previously annealed in vacuum at various temperatures have earlier been reported¹. In all the cases a complete filling-in of the d-band was observed. The present note describes the results for nickel wires annealed at lower temperatures with particular reference to the extent of d-band filling-in:

Sample preparation, annealing procedure, cathodic hydrogen diffusion and thermo emf measurements were as described earlier¹. However, it is appropriate to summarize the interpretation. Figure 1a shows the d-band shape i.e. $n(E)$ vs E curve. The unfilled part of the band lies beyond the Fermi-level. This part of the band gets filled by the electrons donated by the diffused H-atoms. Since the thermo emf is proportional to dn/dE , the curve for this latter function against E is plotted in figure 1b, only for the unfilled part. The process of H-outgassing is just the reverse of filling-in; it will, therefore, start from the higher energy side (T in figure 1a). The mirror image of figure 1b is drawn in



Figures 1a-c. a. Density of state curve for d-band of nickel Flechter (1952). b. dn/dE curve for (a) calculated by numerical differentiation. c. The mirror image of (b).

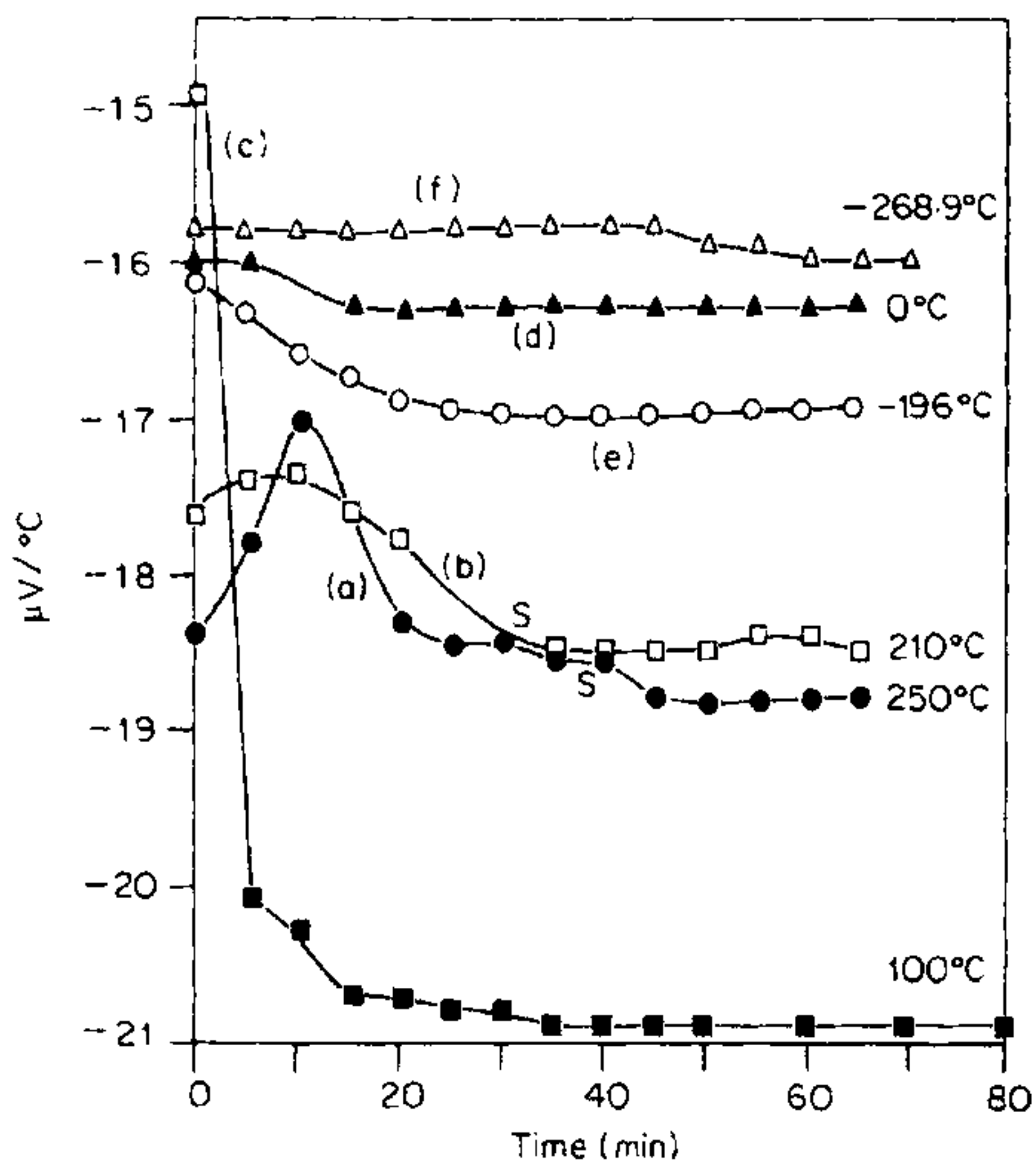


Figure 2. Variation of thermopower of hydrogenated nickel wire annealed at different temperatures.

figure 1c. The curves observed for the variation in thermo emf with time of outgassing reported earlier¹ agree with the shape of the figure 1c except for some extra structures designated by S_1 , S_2 in the experimental curves.

The new results are shown in figure 2. A complete curve of the kind shown in figure 1c is observed only for the 250°C annealed nickel wire. For the rest of the low temperature annealed samples, incomplete curves are the results. Proceeding in the reverse

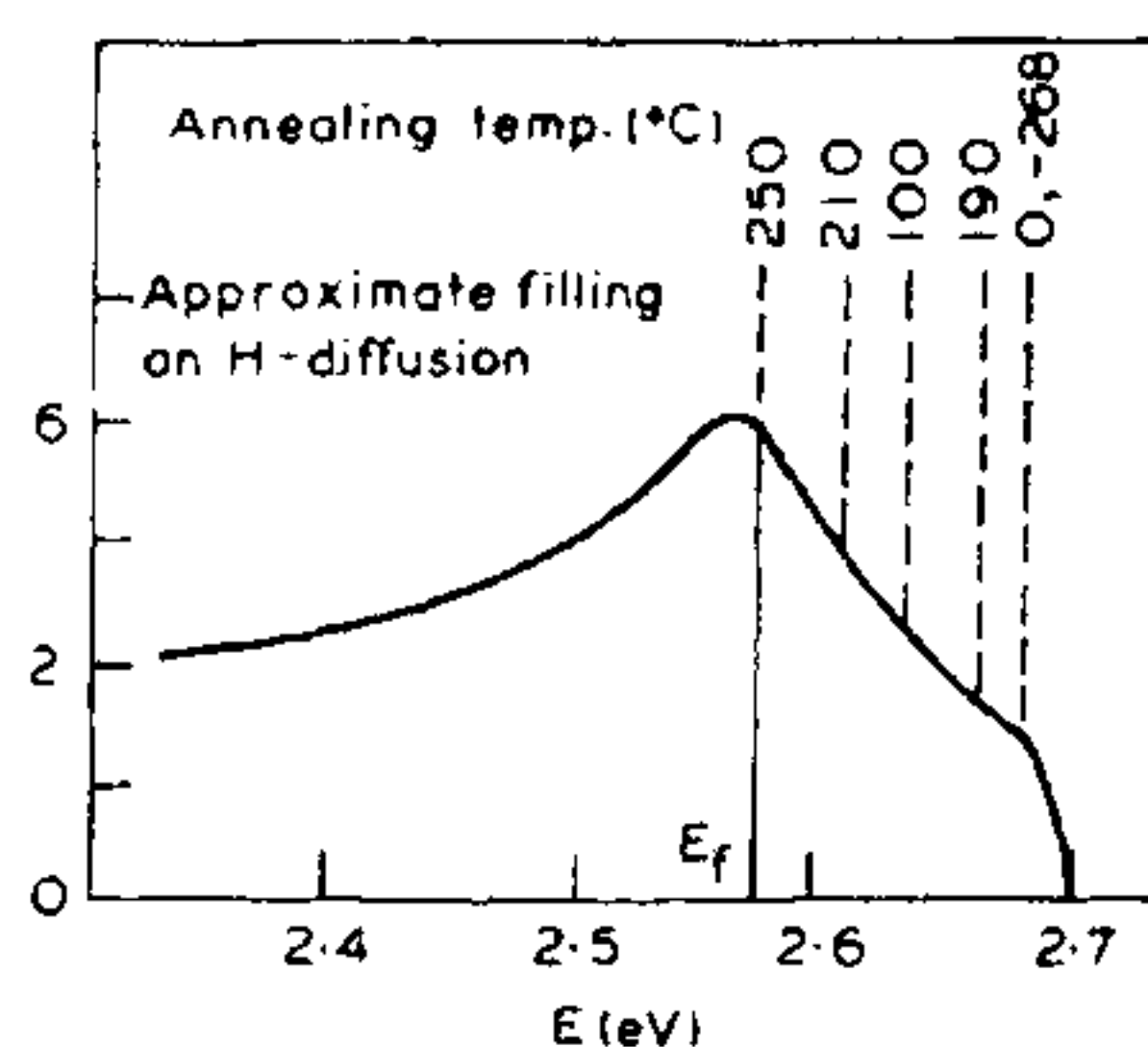


Figure 3. Approximate filling-in of the empty part of d-band on H-diffusion in wires annealed at different temperatures.

order i.e. from figure 1c to 1b to 1a we can arrive at the extent to which the d-band has been filled-in differently annealed wires. These results are shown in figure 3.

The X-ray diffraction patterns of the wires show a change in the orientation factors resulting from annealings at different temperatures.

We also measured² the electrode potentials (e.p.) of these wires dipped in a saturated solution of nickel sulphate with respect to a saturated calomel electrode. The eps of single crystals of nickel with different surfaces [100], [110] and [111] were also measured. It was found² that for a wire annealed at 250°C the ep was expressible as $(ep)_{111} + 2(ep)_{100}$ while for un-annealed wire (equivalent to annealing at 30°C), the ep could be expressed as $(ep)_{111} + (ep)_{100}$. It can therefore be speculated that H-diffusion occurs with greater ease along a direction normal to (100) plane rather than normal to (111) plane.

A further observation is that the annealings at 0°C and at liquid He temperature induce such orientations in the wire that hardly any hydrogen can diffuse in, but the annealing at 0°C creates such orientation that hydrogen diffusion is indeed possible.

The authors thank Dr A. V. Narlikar of NPL, New Delhi for liquid He annealing.

1 May 1986

1. Nigam, A. N. and Garg, V. S., *Phys. Status Solidi.*, 1973, A12, 589.
2. Nigam, A. N. and Gupta, A. C., *Curr. Sci.*, 1984, 53, 1081.